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Off-Gas Adsorption Model and Simulation - OSPREY

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OFF-GAS ADSORPTION MODEL AND SIMULATION - OSPREY

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The absence of industrial scale nuclear fuel reprocessing in the U.S. has precluded the necessary driver for developing the advanced simulation capability now prevalent in so many other countries. Thus, it is essential to model complex series of unit operations to simulate, understand, and predict inherent transient behavior. A capability of accurately simulating the dynamic behavior of advanced fuel cycle separation processes is expected to provide substantial cost savings and many technical benefits. To support this capability, a modeling effort focused on the off-gas treatment system of a used nuclear fuel recycling facility is in progress. The off-gas separation consists of a series of scrubbers and adsorption beds to capture constituents of interest. Dynamic models are being developed to simulate each unit operation involved so each unit operation can be used as a stand-alone model and in series with multiple others. Currently, an adsorption model has been developed within Multi-physics Object Oriented Simulation Environment (MOOSE) developed at the Idaho National Laboratory (INL). Off-gas Separation and REcoverY (OSPREY) models the adsorption of off-gas constituents for dispersed plug flow in a packed bed under non-isothermal and non-isobaric conditions. Inputs to the model include gas composition, sorbent and column properties, equilibrium and kinetic data, and inlet conditions. The simulation outputs component concentrations along the column length as a function of time from which breakthrough data can be obtained. The breakthrough data can be used to determine bed capacity, which in turn can be used to size columns. In addition to concentration data, the model predicts temperature along the column length as a function of time and pressure drop along the column length. A description of the OSPREY model, results from krypton adsorption modeling and plans for modeling the behavior of iodine, xenon, and tritium will be discussed.

I. INTRODUCTION

Modeling and simulations will aid in the future design of U.S. advanced reprocessing plants for the recovery and recycle of actinides in used nuclear fuel. The design of these processes must not only deliver high purity products but also minimize waste, proliferation risk, environmental impact, process complexity, and cost. The Department of Energy Nuclear Energy (DOE NE) Separation and Waste Form Campaign is currently developing a dynamic plant level model that will allow simulations of separation processes for various configurations and operating conditions. This plant model will include the front end of the separations process (dissolution and potential voloxidation of the fuel), the separation processes, and the off-gas treatment system.

An example of the unit operations necessary for the separation of radioactive constituents from off-gas streams consists of an interconnected series of adsorbers for the capture of tritium, Kr, Xe, and I, and scrubbers (absorbers) for the capture of C-14 and NOx as shown in Fig. 1 (Ref. 1).

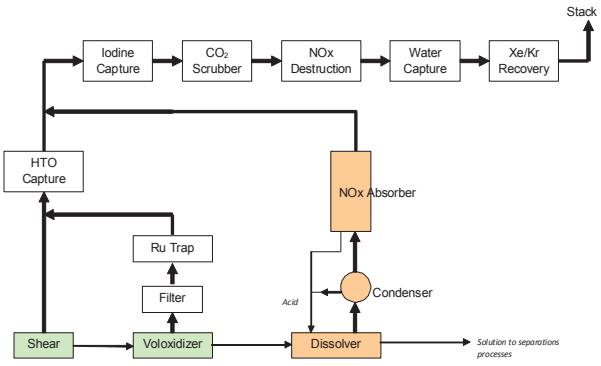

Fig. 1. Schematic of an example off-gas treatment system.

Detailed off-gas modeling requirements were developed in FY 2010. These requirements for the off-gas modeling efforts include the model being dynamic, allowing for various unit operations to be incorporated for comparison and being flexible to allow for variation in unit operation sequencing and the components modeled. Also, each unit operation model will be able to be used as a stand-alone model or in series with other unit operation models.[1] Development of an adsorption model for off-gas treatment systems is the particular area of concern in the work described in this paper.

The objective of the modeling work presented herein was to solve the fundamental transport equations for adsorption in a packed bed in order to obtain a predictive unit operations model for the separation of off-gas constituents.

II. MODELING PLATFORM

An off-gas adsorption model was initially developed using general Process Modeling System (gPROMS) software. The gPROMS approach was described in "Adsorption Model for Off-Gas Separation".[2] The gPROMS platform is an advanced process modeling environment available from Process System Enterprise (PSE). The modeling environment for the off-gas model has been converted from the commercially available gPROMS to INL's MOOSE. This switch was initiated because MOOSE will help expand this model and increase the fidelity of it as modeling efforts continue. Unit operations can easily be coupled utilizing MOOSE. This conversion will allow for greater future flexibility with predictive modeling including 2D and 3D visualization. Using MOOSE for model development will facilitate collaborative usage of the model amongst national laboratories and other entities due to the fact that most of the national laboratories and many other entities are already utilizing MOOSE for modeling and simulation, and therefore, currently have access to it.

MOOSE is a framework for solving computational engineering problems in a well planned, managed, and coordinated way. It was designed to significantly reduce the expense and time required to develop new applications. MOOSE uses very robust linear and non-linear solvers, can be easily extended and maintained, and is efficient on both a few and many processors[3]. This framework provides a core set of functionalities and a modular architecture for coupling of multiple physics. It is built upon Libmesh and solver libraries that provide parallel computing utilities. It has an adaptive mesh refinement capability that enables tremendous savings in solving time. Fig. 2 shows the structure of MOOSE.

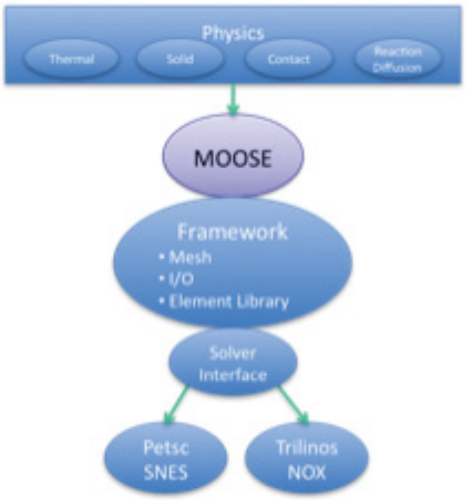

Fig. 2. MOOSE Structure.

Fig. 2 shows that the user input into MOOSE is the physics, MOOSE couples the physics, and the framework that MOOSE is built upon communicates with the solver interfaces to provide a solution. Fig. 3 shows the MOOSE architecture.

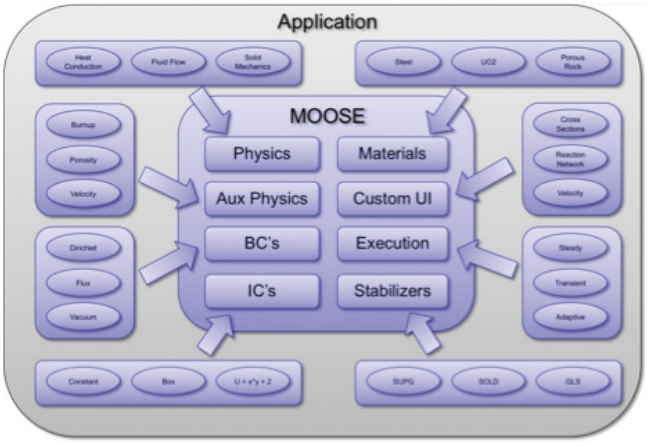

Fig. 3. MOOSE architecture.

The architecture in Fig. 3 shows how the MOOSE framework integrates with an application in order to simultaneously solve the governing equations of the application problem. Each of the titles within the MOOSE bubble, i.e. 'Physics', 'Materials', etc., are the types of information the user provides with their application as inputs for MOOSE. The user can provide multiple of any of the inputs to be coupled within MOOSE. OSPREY is one such application of MOOSE that has been developed to describe and couple the physics of gas adsorption. It fully couples the governing equations and uses the interfaces and solvers provided by MOOSE to simulate the adsorption of off-gas.

A user-friendly interface, which has been developed by the creators of MOOSE, can be used for running MOOSE module simulations. This interface is called Peacock and makes it much easier to run OSPREY and view results, especially for users who are not as accustomed with using MOOSE for running simulations.

III. MATHEMATICAL MODEL

III.A. Assumptions

To develop a generalized model for the adsorption bed, the following assumptions from the off-gas separation process were made:

- Axially dispersed plug flow
- Ideal gas behavior
- No radial concentration gradient
- No radial temperature gradient
- Uniform voidage and particle size
- Thermal equilibrium
- Constant gas velocity

Due to low concentrations of the adsorbing species, large ratio of length to diameter of the column, and larger bed diameter than particle diameter, the assumptions listed above are reasonable.

III.B. Governing Equations

The mass balance describing the concentration gradient of adsorbing species along the adsorption column accounts for the rate of component uptake in the column, the axial dispersion, the convection term, and the rate of mass transfer into the particle. Based on the above assumptions, the mass balance for the adsorbing components is given by equation 1 (Ref. 4).

$$\frac{\partial C_i}{\partial t} = D_{zi}\frac{\partial^2 C_i}{\partial z^2} - v\frac{\partial C_i}{\partial z} - \frac{\rho_b}{\varepsilon}\frac{\partial q_i}{\partial t}; z \in (0, L) \qquad (1)$$

where:
t = time, s
C_i = gas phase concentration of component i, mol/m^3
D_z = axial dispersion coefficient of component i, m^2/s
z = distance from the bed inlet in the axial direction, m
v = superficial gas velocity, m/s
ρ_b = bulk/bed density, kg/m^3
ε = overall bed void, dimensionless
q_i = solid phase concentration of component i, mol/kg
L = bed length, m

The rate of mass transfer into the particle, $\partial q_i/\partial t$, can be described by the linear driving force (LDF) equation, equation 2 (Ref. 4).

$$\frac{\partial q_i}{\partial t} = k_i\left(q_i^* - q_i\right) \qquad (2)$$

where:
q_i^* = equilibrium adsorption amount of component i, mol/kg
k_i = mass transfer coefficient of component i, s^{-1}

The solid phase equilibrium concentrations are represented by the Langmuir equation[4], equation 3 (Ref. 4).

$$q_i^* = \frac{q_{i\max} K_{eq} C_i}{1 + \sum_{i=1}^{n} K_{eq} C_i} \qquad (3)$$

where:
q_{imax} = maximum concentration in the solid phase for component i, mol/kg
K_{eq} = Langmuir equilibrium affinity constant for component i, m^3/mol
n = number of components

The determination of the Langmuir parameters q_{imax}, maximum concentration adsorbed, and K_{eq}, the Langmuir equilibrium constant, will be done by fitting the single component Langmuir equation (n =1) to the experimental adsorption isotherm of component i. The values of the constants for single component adsorption are regarded to be the same as those used for the extended Langmuir, which is used to describe multiple component adsorption.

The pressure distribution along the length of the packed bed is described by equation 4 (Ref. 5).

$$\frac{\partial P}{\partial z} = -K_D v - K_v v^2; z \in (0, L] \qquad (4)$$

where:
P = pressure, Pa
K_D = viscous pressure loss term
K_v = kinetic pressure loss term

For low Reynolds numbers (e.g.<5), the kinetic contribution to the total pressure loss is negligible, and equation 4 reduces to Darcy's law[6].

Equation 5 shows the energy balance[4] for the packed bed for compressible flow.

$$\left(C_{pg}\varepsilon\frac{P}{RT}+\rho_b C_{ps}\right)\frac{\partial T}{\partial t}$$
$$=K_z\frac{\partial^2 T}{\partial z^2}-\nu\varepsilon C_{pg}\frac{P}{RT}\frac{\partial T}{\partial z} \quad (5)$$
$$-\rho_b H_{ad}\frac{\partial q}{\partial t}+\frac{4U_o}{d_c}(T-T_w);z\in(0,L)$$

where:
C_{pg} = gas phase heat capacity, J/(mol*K)
H_{ad} = heat of adsorption of component i, J/mol
C_{ps} = solid phase heat capacity, J/(kg*K)
R = ideal gas constant, J/(mol*K)
T = temperature, K
K_z = effective axial thermal conductivity, W/(m*K)
U_o = overall bed-wall heat transfer, W/(m^2*K)
d_c = column inner diameter, m
T_w = wall temperature, K

The parameters needed for the model, i.e. axial dispersion coefficient, pressure loss terms, etc., are either experimentally determined or estimated using semi-empirical correlations. The parameters that are experimentally determined are discussed more in depth later in this paper. The equations used to estimate parameters, many of which are concentration, temperature, and/or pressure dependent, can be found in Ref. 8.

III.C. Initial and Boundary Conditions

The user must specify initial conditions for gas phase concentration, solid phase concentration, temperature, and pressure. The boundary conditions used to simulate the process are given in equations 6 – 13.

1. Inlet conditions (z = 0)

$$C_i\big|_{z=0}=C_{i,in} \quad (6)$$
$$T\big|_{z=0}=T_{g,in} \quad (7)$$
$$P\big|_{z=0}=P_{in} \quad (8)$$

2. Outlet conditions (z=L)

$$\left.\frac{\partial C_i}{\partial z}\right|_{z=L}=0 \quad (9)$$
$$\left.\frac{\partial T}{\partial z}\right|_{z=L}=0 \quad (10)$$

where:
$C_{i,in}$ = feed concentration of component i, mol/m^3
$T_{g,in}$ = feed gas stream temperature, K
P_{in} = feed gas pressure, bar

The inlet conditions can either be constant or a function of time. The governing equations describing the adsorption process for off-gas separation along with the initial and boundary conditions are coupled and solved in the OSPREY module of MOOSE.

IV. RESULTS AND DISCUSSION

IV.A. Experimental Data for Model Support

In support of the off-gas modeling effort, experimental work has been being performed in conjunction with the modeling work to generate equilibrium data to input into the model. The ongoing krypton adsorption work at the Idaho National Laboratory (INL) has generated two single component isotherms, shown in Fig. 4, for the adsorption of krypton on the INL engineered form of hydrogen mordenite, HZ-PAN.

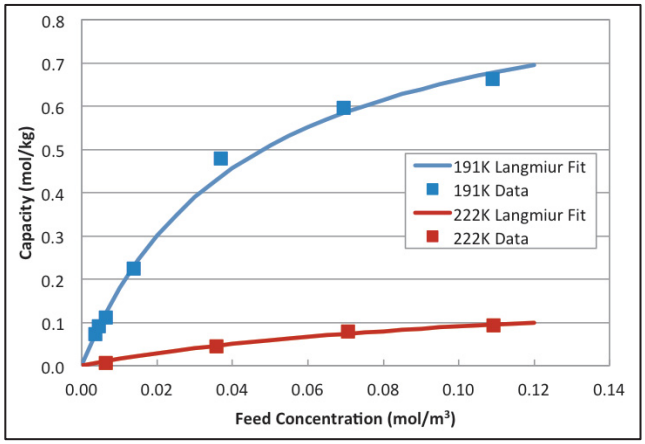

Fig. 4. Isotherms for Kr adsorption on HZ-PAN.

In addition to the experimentally determined isotherms, Fig. 4 shows the Langmuir fit for the experimental data. The Langmuir equation provides a good fit for the data and therefore, validates the assumption that krypton adsorption follows the Langmuir equation, equation 3, where n = 1.

The temperature at which these isotherm data were collected was 190K and 220K, with feed concentrations ranging from 75 ppm to 2544 ppm Kr in helium. The current model is using equilibrium data from the 191 K isotherm and was built based on Kr adsorption on HZ-PAN. The data used for model input are the equilibrium parameters for the Langmuir equation, K_{eq} and q_{max}. These parameters were determined from the

experimentally generated isotherm by fitting the data using the Langmuir linear regression model. The results are shown in Table I.

TABLE I. Equilibrium parameters for Kr adsorption.

	K_{eq}	q_{max}
191 K	0.94	23.4
221 K	0.20	8.4

Having two adsorption isotherms allowed for the estimation for the heat of adsorption for krypton adsorbing on HZ-PAN by using the Clausius-Clapeyron equation, equation 11.

$$\frac{d\left(\ln P_{Kr}\right)}{d\left(1/T\right)} = -\frac{H_{ad}}{R} \qquad (11)$$

where:
P_{Kr} = partial pressure of krypton, Pa

The partial pressure of krypton has to be for the same capacity at each temperature. The resulting heat of adsorption was determined to be 3.84E04 J/mol.

IV.B. Current Adsorption Model

The separation of off-gas constituents modeled in OSPREY by the equations previously described is a single component model that describes the component concentration, gas stream composition, and temperature as functions of bed length and time and pressure as a function of bed length. It is set up to distinguish between inert and adsorbing species involved in the process to obtain the entire gas composition. The model allows for a wide range of user inputs and can easily be scaled up for use in systems larger than a bench scale model. A wide range of parameter dimensions is accepted as input, i.e. column height, various adsorbent properties, and a range of temperatures and velocities.

The reference case used to develop the model is krypton adsorption on an INL engineered form of hydrogen mordenite, referred to as HZ-PAN. The system is starting with an unloaded bed and has a constant concentration inlet stream.

The conversion from gPROMS platform to the MOOSE framework as OSPREY was successfully completed. The outputs of the two modeling environments show decent agreement, as shown in Fig. 5.

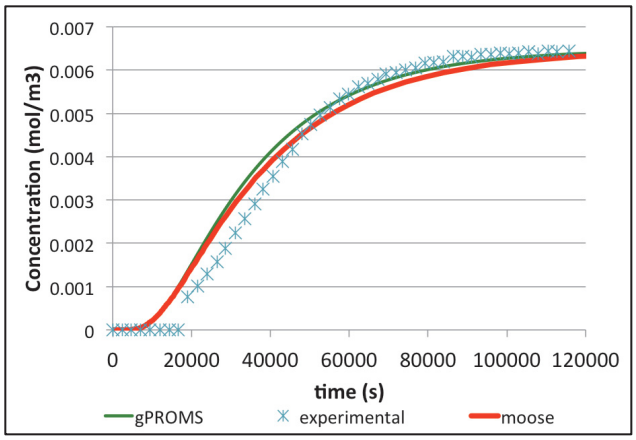

Fig. 5. Comparison of concentration results from experimental work, gPROMS prediction and OPSREY prediction for 150 ppm krypton sorption on HZ-PAN.

The discrepancies are believed to be due to differences in solving methods. In both cases, the default solvers were used to simulate what a general user would obtain. Also, MOOSE utilizes mesh adaptivity so the spacial discretization may differ form the uniform spacial discretization specified in the gPROMS model. The number of time steps is not specified in MOOSE whereas it is in the gPROMS model. In addition, they both show a good agreement with experimental data.

The discrepancies between the models and experimental data are attributed partially to the estimation of the parameters. The axial dispersion coefficient has a large effect on the shifting of the curve, which might account for the difference in when breakthrough occurs. The equilibrium parameters have a large impact on the slope of the middle portion of the breakthrough curve and therefore, if there are not enough experimental data to accurately predict the isotherm, it will greatly impact the slope of the breakthrough curve. However, the predicted curve still gives a good estimate of breakthrough and sorbent capacity. As the parameters are better estimated, more data become available, and further validation is done, this is expected to become a better and tighter fit.

A user-friendly interface, Peacock, has been developed by MOOSE developers and is available for use with OSPREY. This makes it much easier for users of OSPREY to run simulations with their own system specifications. Inputs for the model, which are user specified, include the bed void, sorbent parameters, column specifications, velocity, initial composition, initial temperature, initial pressure, component physical properties, and equilibrium and kinetic parameters. All of these parameters can be specified from within peacock. Fig. 6 shows what peacock looks like.

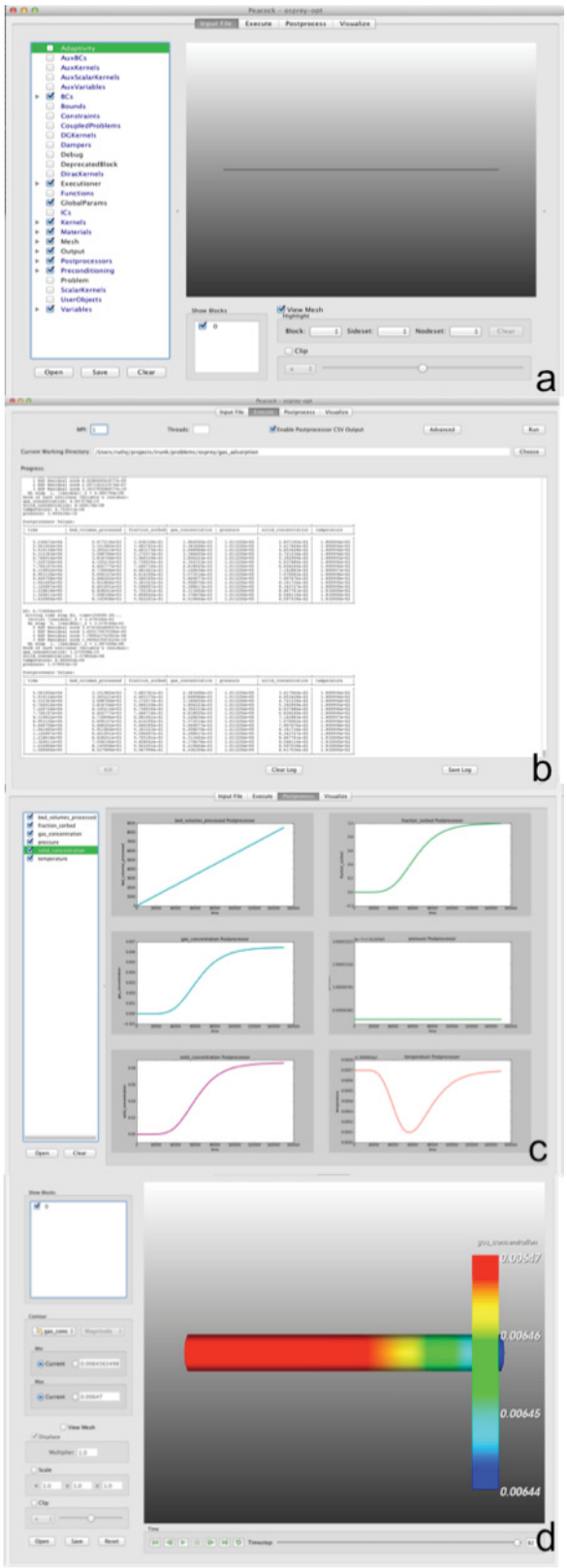

Fig. 6. Image of what each tab within Peacock looks like after running a simulation: 6a. Input file tab 6b. Execute tab 6c. Postprocess tab 6d. Visualize tab.

The tabs within Peacock are, as shown in Fig. 6, input file, execute, postprocess, and visualize. The input file tab (6a) is the tab in which parameters are assigned values. The execute tab (6b) is the tab from which the simulation is ran. This tab will show the last 15 data points that were calculated. The postprocess tab (6c) shows plots of the variables as a function of time. The visualize tab (6d) shows the variable gradient along the bed length as a function of time. This can be played and watched while the simulation is running as well as after the simulation is finished running.

Outputs from the simulation are gas concentration, solid concentration, temperature, pressure, and bed volumes processed at each time step. The results shown in graphical form in the postprocess tab can also be seen in tabular form. These data are also saved as a .csv file that can be opened in excel. A results excel spreadsheet has been developed which will graph these data when copied and pasted from the .csv file into the corresponding columns of the results file. It will graph the breakthrough curve, temperature profile, pressure drop, and concentration profile.

IV.C. Future Adsorption Model Work

The adsorption model has been developed using parameters determined for krypton adsorption on an INL engineered form of hydrogen mordenite, HZ-PAN. Experimentally determined parameters are equilibrium and kinetic parameters. The equilibrium parameters obtained from experimental work are discussed in section IV.A. The kinetic parameters needed for model input are the mass transfer coefficient, seen in equation 2, and any reaction rates, if applicable. A reaction rate is not needed for the krypton adsorption model since physisorption is the only transfer phenomena occurring. Additional versions of the model will be developed for other off-gas constituents (i.e. tritium, iodine, and xenon) as experimental data become available. The current version of the model can be used for single component systems (one adsorbing species in a carrier gas) to which the assumptions listed in section III.A apply.

Other species-specific models that are being considered for the generation of an application within OSPREY are krypton and/or xenon adsorption on an INL engineered form of silver mordenite, tritium adsorption on molecular sieve 3A, and iodine adsorption on silver mordenite. For each species specific model developed, both kinetic and equilibrium data are needed. According to literature, tritium adsorption follows a different equilibrium model. To develop the tritium specific model, a literature search will be performed to obtain the needed experimental data from literature. However, iodine, krypton and xenon adsorption data are not as plentiful in literature as tritium data, therefore, experiments will need to be performed to obtain data for

these models. The iodine specific model may need to include chemical equilibria because iodine sorption is mainly chemisorption.

As stated in the previous section, the model is currently set up for a single adsorbing component in a carrier gas. However, as seen from the subscripts shown on the equations, the model can be expanded to include multiple components that will adsorb. Multi-component experimental testing will be required to complete a multi-component model.

As additional data become available, the model will be further validated and modified. As new versions of the model are completed, they will be saved as a new input file for OSPREY in the MOOSE repository. It will then become available to all OSPREY users when an update is done on their local computer.

V. CONCLUSIONS

In summary, a dynamic fully coupled off-gas adsorption model (OSPREY) has been developed in the MOOSE framework to solve off-gas separation systems of equations simultaneously in a fully implicit manner using finite elements methods. OSPREY will be used as the framework for the reference case unit operation used for capture of iodine, krypton, and xenon off-gas constituents. This generic model has been created for adsorption in a packed bed column with dispersed plug flow.

The adsorption model is currently being used as a stand-alone model but will also be able to be used in series with other unit operation models. The model will continue to be improved and expanded as additional data become available.

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REFERENCES

1. D. HAEFNER, et.al., “System design description and requirements for modeling the off-gas systems for fuel recycling facitilites,” FCRD-MDSM-2010-000134, INL-2010, Idaho National Laboratory (2010).
2. V. J. RUTLEDGE, “Adsorption model for off-gas separation,” FCRD-NEAMS-2011-000069, INL-2011, Idaho National Laboratory (2011).
3. D. GASTON, et.al., “MOOSE Workshop” Training Manual (2012).
4. D. M. RUTHVEN, *Principles of Adsorption Processes,* pp. 225, 317, John Wiley & Sons, NY (1984).
5. W. L. MCCABE, et.al., *Unit Operations of Chemical Engineering*, p. 166, McGraw-Hill, New York, NY (2005).
6. Y. DING, et.al., “Equilibria and kinetics of CO_2 adsorption on hydrotalcite adsorbent,” *Chem. Eng. Sci*., **55** (2000).
7. A. MALEK, et.al., “Determination of equilibrium isotherms using dynamic column breakthrough and constant flow equilibrium desorption,” *J. Chem. Eng. Data*, **41**, 1 (1996).
8. V. J. RUTLEDGE, “OSPREY Model,” FCRD-SWF-2013-000086, INL-2013, Idaho National Laboratory (2013).